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(54) Title: PHOTO-CURABLE VINYL ETHER COMPOSITIONS

(57) Abstract

A liquid composition curable by exposure to light of appropriate wavelength, such as ultraviolet light, is a homogeneous liquid containing both vinyl ether groups and maleate or fumarate groups in the presence of a hydrogen or alkoxyl-functional ac-
tophenone derivative or a benzoyl diaryl phosphine oxide photoinitiator. These compositions are free from residues of cationic
curing catalysts, which cause discoloration and sensitivity to water. Coated metals are better protected against corrosion. Other
utilities include use in serodiagnostics, dentistry, lamination of glass and other films and pretension processes.

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H.N. WELLS

V.C. Ethen form. vinyl polymer

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PHOTO-CURABLE VINYL ETHER COMPOSITIONS

DESCRIPTION

Technical Field

This invention relates to photo-curable vinyl ether compositions having improved cure speed when exposed to light of appropriate wavelength. Coatings are primarily contemplated.

Background Art

It is known that vinyl ethers cure rapidly when exposed to ultraviolet light in the presence of a cationic curing catalyst. Unfortunately, the cure under cationic conditions leaves catalyst residues which discolor the cured films and cause them to be sensitive to water. Metals coated with such cured films are not adequately protected against corrosion.

A rapid cure on ultraviolet exposure providing better cured films is obtained using (meth)acrylates in the presence of photoinitiators which can be described as ketonic photoinitiators. However, (meth)acrylates are generally hazardous to human health, so it is desired to eliminate these wherever possible. Vinyl ethers are much less toxic than (meth)acrylates, but vinyl ethers do not cure when exposed to ultraviolet light in the presence of ketonic photoinitiators. Similarly, unsaturated polyesters containing maleic or fumaric unsaturation are known to be non-toxic, but while these will cure when exposed to ultraviolet light in the presence of ketonic photoinitiators, the cure is unacceptably slow.

While various ketonic photoinitiators are available, and while some of these are better than others in different situations, acetophenones are generally similar to the other ketonic

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photoinitiators. I know of no reason in the art why hydroxy or alkoxy-functional acetophenone derivatives, and more particularly hydroxyalkyl phenones, should behave differently with respect to vinyl ethers. Similarly, no reason is known why benzoyl diaryl phosphine oxides, which are also known photoinitiators, should behave differently with respect to vinyl ethers. Nonetheless, the specified photoinitiators are uniquely effective in the combinations which are the subject of this invention.

Summary of Invention

In accordance with this invention, a homogeneous liquid composition curable by exposure to light of appropriate wavelength, such as ultraviolet light, contains both vinyl ether groups and maleate or fumarate groups in the presence of an hydroxy or alkoxy-functional acetophenone derivative, preferably an hydroxyalkyl phenone, or a benzoyl diaryl phosphine oxide, as photoinitiator. These two different types of ethylenic unsaturations interact rapidly in the presence of the specified photoinitiators to provide a rapid photocure. This is a surprising and important finding, and I do not know why this is so.

More particularly, and using ordinary aryl ketone photoinitiators, such as benzophenone, maleate and fumarate-functional materials respond poorly to photocure using, for example, ultraviolet light. Under these same conditions the vinyl ethers do not exhibit any substantial responses to the ultraviolet exposure. Nonetheless, these two types of unsaturation in admixture respond to the photocure very rapidly when the photoinitiator is correctly selected. The photocure is especially rapid and

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effective when both of the described functionalities are provided in polyfunctional moieties, particularly those of resinous character. The fastest cures are obtained when the respective functionalities are present in about the same equivalent amount.

In the usual practice of this invention, the homogeneous liquid composition comprises a blend of a vinyl ether compound, preferably an oligomer containing a plurality of vinyl ether groups, and a maleic or fumaric-unsaturated ester, preferably a polyester containing a plurality of maleate or fumarate groups, and especially a resinous polyester which is of liquid character so as to minimize the need for diluents to reduce viscosity and thus enable coating application. The photoinitiator is usually added shortly prior to use, but this is not essential.

The term "liquid", and any other term used herein to describe the physical condition of anything, is used in its normal sense to denote the condition at room temperature (about 25 C). The vinyl ether compound and the maleic or fumaric-unsaturated ester are either liquids themselves or in admixture, or if the mixture is not sufficiently flowable for the intended use, such as coating application, then other liquid components are added to provide the desired viscosity.

Detailed Description of Invention

The vinyl ether compounds which may be used herein are subject to wide variation, vinyl ether monomers, like butyl vinyl ether and octyl vinyl ether being useful. These monomers are volatile, and it is preferred to use the higher molecular weight vinyl ethers which are less volatile. The vinyl ether

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compounds which are preferred are oligomeric and contain more than one vinyl ether group per molecule. To illustrate polyvinyl ether oligomers, one may use the bisvinyl ether of triethylene glycol or of any other diol, such as 1,6-hexane diol or

5 dibutylene glycol. One may also use polyvinylates of other polyhydric alcohols, such as glycerin or trimethylol propane. Polyhydric polyethers can be used, such as ethylene oxide, propylene oxide or butylene oxide adducts of polyhydric alcohols, illustrated by ethylene glycol, butylene glycol, glycerin, trimethylol propane or pentaerythritol. Polyvinyl ether polyurethanes of the type shown in U.S. Pat. No. 4,751,273 are also useful.

10 Liquid polyvinyl ethers are preferred for low viscosity, albeit ethylenic monomers, like n-butyl vinyl ether or monobutyl or dibutyl maleate or fumarate or volatile organic solvents may be used to reduce viscosity when this is desired.

20 The polyethylenic maleic or fumaric polyesters are preferably liquid hydroxy functional linear polyesters resins having an acid value of less than about 30.

The molecular weight of the polyester is determined by the ratio of hydroxyl to carboxyl groups. A ratio of about 2:1 or higher provides a low molecular weight while a ratio of about 1:1 provides high molecular weight. The extent of

30 reaction also influences molecular weight, the low acid value products used herein indicating relatively complete reaction. Maleic and fumaric acids are dicarboxylic (maleic anhydride is also useful), and they are usually reacted with a diol, such as ethylene glycol, propylene glycol, or other diol as illustrated herein, to provide the

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polyester. A ratio in the range of from 1.1:1.0 to 1.4:1.0 is preferred. Polyols containing more than two hydroxy groups may be present in small amounts, such as up to about 25% of total hydroxy functionality of trimethylol propane to provide branching in the otherwise linear polyester.

The lowest molecular weight materials are useful herein, albeit some of these are volatile and hard to use for that reason. Nonetheless, the difficulty of handling volatile materials does not prevent the rapid cure which is achieved herein. Similarly, higher molecular weight makes it more difficult to provide a homogeneous liquid composition, but the presence of monomeric unsaturated liquid diluents and volatile organic solvents can extend the molecular weights of the components which can be combined in a homogeneous liquid composition. So long as the composition is a homogeneous liquid, it can be used herein.

The blend of vinyl ether compound and maleic or fumaric-unsaturated polyester may vary considerably from a weight ratio of 5:95 to 95:5. However, it is preferred to employ a weight ratio of from 20:80 to 80:20. Best results are obtained using a weight ratio of from 35:65 to 65:35. As should be evident, an exact balance between the two types of unsaturated groups is not essential in this invention.

While useful results are obtained without a precise balance between the vinyl ether groups and the maleate or fumarate groups, the fastest and best cures are obtained when these two groups are present in about stoichiometric proportions. Thus, the cure speed falls off badly when the equivalent ratio of the two types of groups is outside the range of

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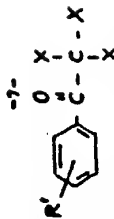
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about 3:1 to about 1:3, preferably 2:1 to 1:2.

It is desired to point out that in the usual situation one blends a vinyl ether-functional material and a maleate or fumarate-functional material together into a homogeneous liquid composition to which is added, at any convenient time, the selected photoinitiator. However, these two separate functionalities may be present in the same oligomeric molecule.

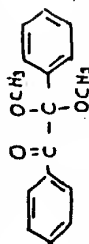
To illustrate using the same molecule to support both types of unsaturations, one may provide the vinyl ether group in the compound hydroxybutyl vinyl ether. Maleic anhydride can be adducted with butyl alcohol to form monobutyl maleate which is then adducted with a molar proportion of propylene oxide to form 2-hydroxypropyl monobutyl maleate. One mole of hydroxybutyl vinyl ether and one mole of 2-hydroxypropyl monobutyl maleate can then be reacted with one mole of an organic diisocyanate, like isophorone diisocyanate. This reaction is preferably carried out in two stages so that all of one of the two unsaturated compounds bonds with the more reactive isocyanate group on the diisocyanate, and then the second unsaturated compound is added to react with the remaining isocyanate group. The result is a polyurethane formed in conventional manner using catalysts such as dibutyl tin dilaurate and temperatures of about 30 C in the first stage and 60 C in the second stage. This polyurethane contains vinyl ether groups and maleate groups in the same molecule, and these can be cured by appropriate light exposure in accordance with this invention.

The acetophenone derivatives which may be used have the formula:

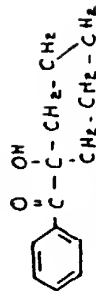


in which R' is an optional hydrocarbon substituent containing from 1 to 10 carbon atoms and which may be alkyl or aryl, e.g., methyl, ethyl, butyl, octyl or phenyl, X is selected from the group consisting of hydroxy, C₁-C₆ alkoxy, C₁-C₆ alkyl, cycloalkyl, halogen, and phenyl, or 2 Xs together are cycloalkyl, and at least one X is selected from hydroxy and C₁-C₆ alkoxy.

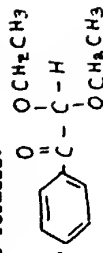
All sorts of compounds have the required structure. Thus, the alkoxy groups are preferably methoxy or ethoxy, the alkyl group is preferably methyl or ethyl, the cycloalkyl group is preferably cyclohexyl, and the halogen is preferably chlorine. Only a few of the useful compounds are available in commerce. Thus, one can use the Ciba-Geigy product Irgacure 651 which has the formula:



Irgacure 184 is another useful acetophenone derivative, and it has the formula:



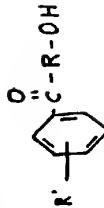
Still another commercially available useful acetophenone derivative is diethoxy acetophenone which has the formula:



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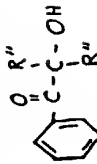
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When the photoinitiator is an hydroxy-functional compound, one can define the useful acetophenone derivatives in a somewhat different manner. Thus, the hydroxyalkyl phenones which are preferred herein have the formula:



in which R is an alkylene group containing from 2-8 carbon atoms and R' is an optional hydrocarbon substituent containing from 1 to 10 carbon atoms and which may be alkyl or aryl, e.g., methyl, ethyl, butyl, octyl or phenyl.

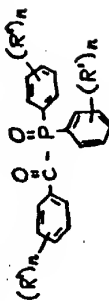
It is particularly preferred that the hydroxy group be in the 2 position in which case it is preferably a tertiary hydroxy group which defines an hydroxy group carried by a carbon atom which has its remaining three valences connected to other carbon atoms. Particularly preferred compounds within which will be found the commercial material used to obtain the data discussed have the formula:



in which R'' is an alkyl group containing from 1 to 4 carbon atoms. In the commercial product Darocur 1173, each R'' is methyl. This provides a compound which can be described as 2-hydroxy, 2-methyl, 1-phenyl propane 1-one. The corresponding compound in the term "propane" is replaced by butane or hexane, and these will further illustrate preferred compounds in this invention.

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The benzoyl diaryl phosphine oxide photoinitiators which may be used herein have the structure:



In the above formula, R' is an optional

hydrocarbon substituent containing from 1 to 10

carbon atoms and which may be alkyl or aryl as

previously noted, and n is an integer from 1 to 3.

In preferred practice, a 2,4,6-trimethyl benzoyl

compound is used, and the two aromatic groups

connected to the phosphorus atom are phenyl groups.

This provides the compound 2,4,6-trimethyl benzoyl

diphenyl phosphine oxide which is available from

BAEP under the trade designation Lucerin.

When solvent is used, it is usually desired to

allow most of the solvent to vaporize before the

deposited coating is cured by exposure to light, but

this is not essential, especially when the solvent

proportion is small.

The viscosity-reducing liquids are illustrated by

reactive diluents, such as monomeric vinyl ethers

(ethyl vinyl ether or butyl vinyl ether) or

monomeric maleates (like monobutyl maleate or

dibutyl maleate). Inert diluents, like volatile

organic solvents (methyl ethyl ketone, acetone,

butyl acetate, or 2-ethoxy ethanol) are also useful

to reduce viscosity, albeit these are preferably

evaporated prior to light exposure, as has been

noted.

It is stressed that vinyl ethers do not cure when

exposed to ultraviolet light in the presence of

ordinary ketonic photoinitiators, such as

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benzophenone. Similarly, unsaturated polyesters in which the unsaturation is provided by the maleate or fumarate group cure slowly and unsatisfactorily when exposed to ultraviolet light in the presence of

ketonic photoinitiators, such as benzophenone.

Interestingly, a mixture of these two components is

also curable on ultraviolet light exposure in the

presence of a conventional ketonic photoinitiator,

such as benzophenone. While the cure of such

mixtures is still unacceptably slow, I have found it

to be faster than one might suspect from the actions

of the two separate components.

However, when the ketonic photoinitiator is

selected to be an hydroxyalkyl phenone

photoinitiator, then the cure of the mixture is

quite rapid and useful, as will be illustrated.

While the compositions of this invention are

useful when the named components are the only ones

present, other saturated and unsaturated materials

may also be present. Thus, volatile solvents may be

present as well as saturated and unsaturated resins

of various type, such as linoleic acid-modified

saturated polyesters. It is preferred not to have

acrylate-functional materials present, for these

introduce toxicity problems which are largely

avoided by this invention.

A composition was formulated to contain 20 parts

by weight of a bisvinyl ether of triethylene glycol,

22.8 parts by weight of a polyester made by reacting

1.5 moles of maleic anhydride with 1.8 moles of 1,5-

pentene diol to an acid value of 10, at which point

the unsaturated polyester is a viscous liquid at

room temperature. The ratio of vinyl ether groups

to maleate groups in this composition is about 1:1.

When a photoinitiator was added to this composition

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it was added in a proportion of about 0.5% by weight. It is noted that all parts and proportions herein are by weight, unless otherwise specified.

The described composition in the absence of added initiator was coated on an aluminum substrate by drawing it down with a #40 wire wound rod and the wet coating was exposed to ultraviolet light of about 300 nanometers in wavelength. Three exposures were used, namely: 1, 2, and 3 J/cm². A full cure using only 1 J/cm² represents a desirable cure rate, whereas 3 J/cm² is too slow for commercial use.

The uncatalyzed mixture was stable in the dark for more than two weeks, and thus is satisfactorily stable, but in the absence of added initiator no cure was observed on any of the three ultraviolet exposures.

The described composition was then catalyzed with benzophenone. A slight cure was observed at the 2 Joule level, but even using 3 Joules which produced significant resistance to methyl ethyl ketone solvent, the film was cheesy and unsatisfactory.

Michler's ketone (tetramethyldiaminobenzhydrol) was then substituted for the benzophenone. The cure at the 2 Joule level was slightly better than with benzophenone, but the film was still cheesy at the 3 Joule exposure level.

Naphthalene was then tried as the catalyst, but no activity was seen.

A 50:50 catalyst mixture was then used in which Michler's ketone was combined with a cationic curing catalyst (a sulfonium cationic catalyst supplied by General Electric under the trade designation GE-UVE 1014). This product is a commercial cationic catalyst known to be useful for curing vinyl ethers.

The cure was rapid, producing significant solvent

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resistance at the 1 Joule exposure level. However, the cured film was very dark and cratered, and hence unsatisfactory. This illustrates how the conventional cationic cure is not acceptable, albeit such a cure is quite rapid.

2-hydroxypropyl phenone in which the hydroxy group is a tertiary hydroxy group is a known photoinitiator available under the trade designation Darocur 1173 from the E-M Company, Hawthorne, NY). This photoinitiator was used in an amount of 4% based on the weight of the composition to cure the described composition. A full cure was obtained at the 1 Joule exposure level. The cured film was clear and continuous and possesses significant resistance to methyl ethyl ketone solvent. This represents a rapid cure to obtain a useful cured film, and is quite surprising in the light of the various failures which have been reported.

Replacing 2-hydroxypropyl phenone with an equal weight of 2,4,6-trimethyl benzoyl diphenyl phosphine oxide, similar outstanding results were obtained.

In contrast, and using 4% of Darocur 1173 to try to cure the triethylene glycol divinyl ether by itself, no cure was obtained using up to 3 Joules of ultraviolet exposure. Using 4% of Darocur 1173 to try to cure the maleate polyester, the film was tacky until 3 Joules of ultraviolet exposure had been applied. This represents a slow cure since three times the exposure was needed in comparison with the presence of both unsaturated groups.

The light used for cure in this invention can have a wavelength anywhere in the ultraviolet range, including visible light close to that range. This broadly identifies wavelengths which are shorter than 600 nanometers, preferably shorter than 400

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nanometers (usually 200-350 nanometers).
 Monomeric components which are appropriately unsaturated are presently viewed as the best materials with which to reduce any excessive viscosity which may be present. These are illustrated by vinyl ether, such as ethyl vinyl ether, propyl vinyl ether and butyl vinyl ether, other less volatile materials are preferred, like octyl vinyl ether or butylene glycol divinyl ether. Similarly, one can have present simple maleates and fumarates, such as a C₄-C₈ ester of maleic or fumaric acid, such as monobutyl maleate or monooctyl fumarate. Simple dimaleates, such as glycerin dimaleate or butane diol dimaleate may also be present. One may also employ up to about 10% of allylic monomers or oligomers containing the same, like diallyl succinate or diallyl adipate. Even styrene or vinyl toluene may be present to reduce viscosity. Regardless of the presence of these additional components, the hydroxyalkyl phenones enhance the light-activated cure of liquid compositions containing both vinyl ether groups and maleic or fumaric unsaturation.

When the polyvinyl ether and the polyester possess excessive viscosity, it is preferred to employ up to 40%, preferably from 5% to 25%, of the above-described liquid monomers based on the weight of the composition, but these are not essential.

It is preferred, as illustrated, to employ a homogeneous liquid mixture of a polyvinyl ether and a linear polyester having a plurality of maleate or fumarate groups. These polyesters are preferably formed by polyesterifying maleic acid or anhydride or fumaric acid with a dihydric alcohol containing from 2-8 carbon atoms to an acid number of less than

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30. Such liquid mixture can be sold without the photoinitiator which is added by the user prior to coating application and exposure to light of appropriate wavelength, e.g., ultraviolet light.

Some further tests were made using the polyvinyl ether-maleic polyester mixture described previously, but using 3% of photoinitiator. A full cure to 100 MEK double rub resistance was had using Darocur 1173 on an exposure of only 0.5 Joules per sq. cm. Using Irgacure 651, Irgacure 184 and diethoxy acetophenone, the stated full cure required twice the exposure (1 Joule per sq. cm). In two of these instances, some slight rub off was observed, so the cure was slightly inadequate. Other photoinitiators were less satisfactory, illustrated by benzophenone which cured to less than 100 MEK double rub resistance using 2 Joules per sq. cm.

Changing proportions to 2:1, the results were almost as good regardless of which of the two components was in excess. Some inadequacies in the cure began to show up using proportions of 3:1, and the cure performance degrades further when the equivalent proportions are further out of balance.

While coating application is primarily intended herein, other utilities, such as use in stereolithography, dentistry, lamination of glass and other fibers, and protrusion processes, are also contemplated.

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WHAT IS CLAIMED IS:

1. A photocurable liquid composition, said composition being a homogeneous liquid containing both vinyl ether groups and maleate or fumarate groups in the presence of an hydroxy or alkoxy-functional acetophenone derivative or a benzoyl diaryl phosphine oxide as photoinitiator.
2. A liquid composition as recited in claim 1 in which said composition comprises a blend of a polyvinyl ether oligomer and a maleic or fumaric-unsaturated polyester present in a weight ratio of 5:95 to 95:5.
3. A liquid composition as recited in claim 2 in which said unsaturated polyester is an hydroxy-functional liquid resin having an acid value of less than 30 and said polyvinyl ether oligomer and said unsaturated polyester are present in a weight ratio of from 20:80 to 80:20.
4. A liquid composition as recited in claim 3 in which said unsaturated polyester is an hydroxy-functional liquid having an acid value of less than 30 and said vinyl ether compound and said unsaturated polyester are present in a weight ratio of from 35:65 to 65:35.
5. A liquid composition as recited in claim 1 in which said photoinitiator has the formula:



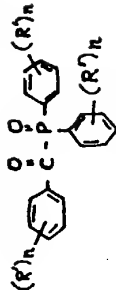
- in which R' is an optional hydrocarbon substituent containing from 1 to 10 carbon atoms, and X is selected from the group consisting of hydroxy, C₁-C₄ alkoxy, C₁-C₄ alkyl, cycloalkyl, halogen, and phenyl, or 2 Xa together are cycloalkyl, at least one X

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- being selected from hydroxy and C₁-C₄ alkoxy.
6. A liquid composition as recited in claim 5 in which said polyester is a maleic acid, maleic anhydride or fumaric acid polyester with a dihydric alcohol containing from 2-8 carbon atoms in a ratio of hydroxy groups to carboxyl groups of from 1:1.1:1.0 to 1.4:1.0 and having an acid number of less than 30.
7. A liquid composition as recited in claim 5 in which the equivalent ratio of the vinyl ether and maleate or fumarate groups is in the range of about 3:1 to about 1:3.

8. A liquid composition as recited in claim 1 in which said photoinitiator has the formula:



- in which R' is an optional hydrocarbon substituent containing from 1 to 10 carbon atoms and n is an integer from 1 to 3.
9. A liquid composition as recited in claim 7 in which the hydroxy group in said formula is in the 2 position with respect to the carbonyl group in said formula and the hydroxy group in said formula is a tertiary hydroxy group.
10. A liquid composition as recited in claim 8 in which said photoinitiator is the compound 2,4,6-trimethyl benzoyl diphenyl phosphine oxide.
11. A method of coating a substrate comprising, applying the mixture of claim 1 as a film upon a substrate, and then exposing said film to light in or near the ultraviolet range to cure the same.

AMENDED CLAIMS

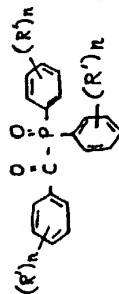
[revised by the International Bureau on 29 January 1990 (79.01.90)
original claims 6-10 amended; other claims unchanged (1 page)]

being selected from hydroxy and C₁-C₆ alkoxyl.

6. A liquid composition as recited in claim 5 in which said polyester is a maleic acid, maleic anhydride or fumaric acid polyester with a dihydric alcohol containing from 2-8 carbon atoms in a ratio of hydroxy groups to carboxyl groups of from 1:1.1:0 to 1.4:1:0 and having an acid number of less than 30.

7. A liquid composition as recited in claim 5 in which the equivalent ratio of the vinyl ether and maleate or fumarate groups is in the range of about 3:1 to about 1:3.

8. A liquid composition as recited in claim 1 in which said photoinitiator has the formula:



in which R' is an optional hydrocarbon substituent containing from 1 to 10 carbon atoms and n is an integer from 1 to 3.

9. A liquid composition as recited in claim 8 in which said photoinitiator is the compound 2,4,6-trimethyl benzoyl diphenyl phosphine oxide.

10. A method of coating a substrate comprising, applying the mixture of claim 1 as a film upon a substrate, and then exposing said film to light in or near the ultraviolet range to cure the same.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/02931

A CLASSIFICATION OF SUBJECT MATTER is given (indicating technical field, sub-field, etc.)

IPC⁸ C08G 63/76 C08L 67/02 G03C 1/727, 5/ 04

INT. CL. 525/44 522/107, 14, 44, 90, 913 430/281, 285, 494

A PRIOR DATES

Classification Symbol

Classification Symbol

522/107, 14, 44, 90, 913

525/44

430/281, 285, 494

Classification Symbol

Classification Symbol

APR 15 NOV. 88 HYDROXYALKYLPHENONE; VINYLETHYR

IN DOCUMENTS REFERRED TO BY THIS REPORT

Category 1: Cations of Document, 11 with indication, where appropriate, of the relevant paragraph 12

Referenced to Claim No. 12

X US, A 4,447,520 (HENNE ET AL) 08 MAY 1984

SEE COLUMN 1, LINES 28-38,

COLUMN 2, LINES 1-68 AND COLUMN

3, LINES 11-14.

1-3, 7, 9

X US, A 4,721,734 (GELHAUS ET AL)

26 JANUARY 1988

SEE COLUMN 4, LINES 45-53,

COLUMN 7, LINES 42-47 AND

COLUMN 8, LINES 9-14.

1-5, 10

* Special categories of cited documents: 8

* "A" documents defining the general state of the art which is not

* "B" documents defining the state of the art which is not

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* "U" documents defining the state of the art which is not

* "V" documents defining the state of the art which is not

* "W" documents defining the state of the art which is not

* "X" documents defining the state of the art which is not

* "Y" documents defining the state of the art which is not

* "Z" documents defining the state of the art which is not

* "AA" documents defining the state of the art which is not

* "AB" documents defining the state of the art which is not

* "AC" documents defining the state of the art which is not

* "AD" documents defining the state of the art which is not

* "AE" documents defining the state of the art which is not

* "AF" documents defining the state of the art which is not

* "AG" documents defining the state of the art which is not

* "AH" documents defining the state of the art which is not

* "AI" documents defining the state of the art which is not

* "AJ" documents defining the state of the art which is not

IV. CERTIFICATION

Date of the Actual Completion of the International Search

11 OCTOBER 1989

International Searching Agency/ly

JSA/US

SUSAN BERMAN

SUSAN BERMAN

Date of Mailing of the International Search Report

14 NOV 1989

Signature of Authorizing Officer

SUSAN BERMAN

SUSAN BERMAN

Form PCT/US89/02931 (Rev. 11-87)

IN DOCUMENTS REFERRED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category	Category of Document, with indication, where appropriate, of the relevant paragraph	Referred to Claim No.
Y	U.S., A 4,606,994 (ILLERS ET AL.) 19 AUGUST 1986 SEE COLUMN 7, LINE 29 TO COLUMN 8, LINE 3.	1-3, 5
Y	U.S., A 4,200,762 (SCHMIDLE) 29 APRIL 1980 SEE COLUMN 5, COLUMN 4, LINES 13-40 AND COLUMN 3, LINE 51 TO COLUMN 4, LINE 9.	1-3, 5, 10
A	U.S., A 4,265,723 (HESSE ET AL.) 05 MAY 1984 SEE COLUMN 546.	1-3, 7, 9
A	U.S., A 4,434,035 (EICHLEN ET AL.) 28 FEBRUARY 1984 SEE COLUMN 5, LINE 20.	1-3, 5

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3. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(b) (4) for the following reasons:

- ☐ Claim numbers: because they were not required to be searched by this Authority, namely:

- ☒ Claim numbers: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out (1), specifically:

THE FORMULA OF CLAIM 7 DOES NOT INDICATE A HYDROXYL GROUP
IN THE 2 POSITION WITH RESPECT TO THE CARBOXYL GROUP.
THE DESCRIPTION MAY BE APPLICABLE TO THE FORMULA IN CLAIM 5.

- ☐ Claim numbers: because they are dependent claims not entitled to examination with the parent and first sentences of PCT Rule 1.4(c).

4. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

The International Searching Authority found multiple inventions in this international application as follows:

- ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

- ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

- ☐ The required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims. It is covered by claim numbers:

- ☐ As all searchable claims could be searched without effort paying an additional fee, the International Searching Authority is not required to pay additional fee.

- ☐ The additional search fees were accompanied by applicant's protest.

- ☐ The protest accompanied the payment of additional search fees.